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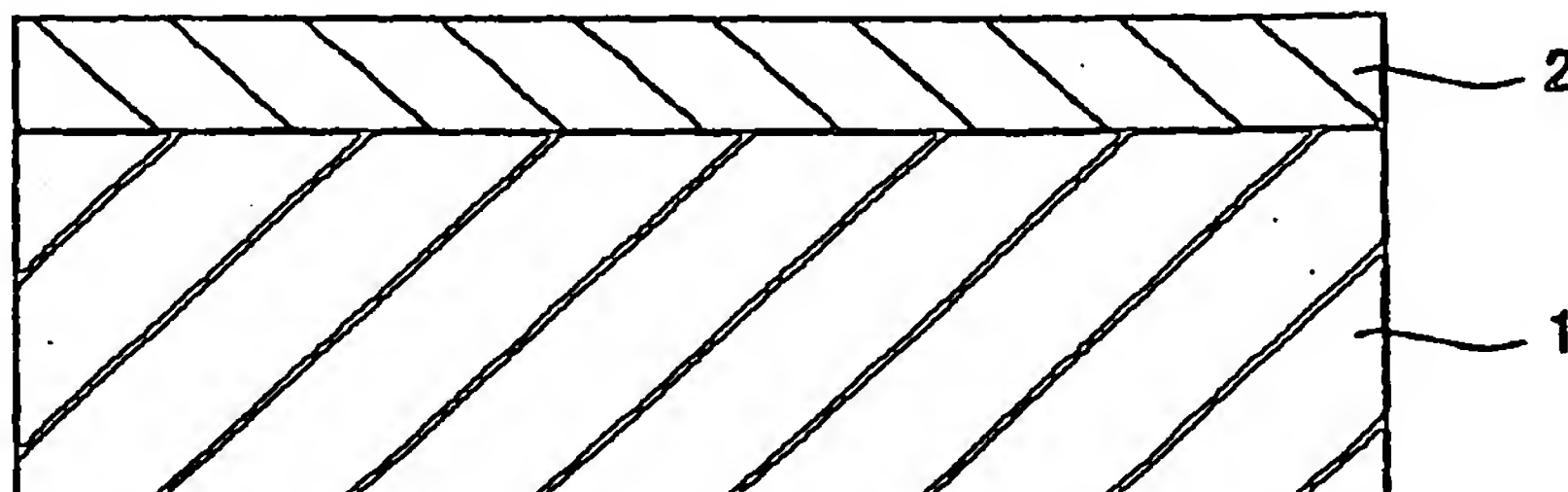
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(54) HYDROGEN-PERMEABLE STRUCTURE AND METHOD FOR PREPARATION THEREOF

(57) A hydrogen permeable structure includes a base material (1) including porous ceramic, and a hydrogen permeable film (2) formed on the base material (1), including palladium (Pd) and at least one element other than palladium and having an amount of hydrogen

dissolution at a prescribed temperature smaller than that of palladium alone. The hydrogen permeable film (2) is formed on the surface of the base material (1) including the porous ceramic by a physical vapor deposition technique.

FIG.1



EP 1 342 500 A1

Description

Technical Field

[0001] The present invention generally relates to a hydrogen permeable structure and a method of manufacturing the same, and more particularly, to a hydrogen permeable structure in which a hydrogen permeable film is formed on a porous base material and a method of manufacturing the same.

Background Art

[0002] Hydrogen gas is used as a fuel for a fuel cell and the like, and is manufactured by e.g. a method of transforming gaseous fuel. For instance, according to the method of transforming gaseous fuel, water vapor is reformed to produce hydrogen gas, the reformed gas including, in addition to hydrogen as a principal component, carbon monoxide, carbon dioxide and the like as sub components. If the reformed gas is used as it is for a fuel cell, the cell is deteriorated in performance. Thus, there is a need for removing sub components, i.e. components other than hydrogen, to refine the reformed gas in order to obtain hydrogen gas with high purity. One of refining methods is to utilize a characteristic of the hydrogen permeable film that selectively allows only hydrogen to pass therethrough. For use, the hydrogen permeable film is formed on a porous support or base material.

[0003] For instance, Japanese Patent Laying-Open No. 11-267477 has proposed a hydrogen permeable structure in which a hydrogen permeable film such as a Pd film, Nb film or the like having a thickness of approximately 0.1 to 20 μm is formed by an ion plating technique on the surface of a porous support made of stainless steel or ceramic such as alumina and silicon nitride.

[0004] Moreover, Japanese Patent Laying-Open No. 11-286785 has proposed a hydrogen permeable structure in which Pd metal and metal to be alloyed with Pd are alternately layered on the surface of a porous support by an electroless plating technique or the ion plating technique, which is subsequently subjected to a heating process, to form a Pd alloy film as a hydrogen permeable film.

[0005] Furthermore, Japanese Patent Laying-Open No. 4-349926 has proposed a hydrogen gas separation film in which silica gel having an average pore diameter of 10 to 30 \AA , alumina gel having an average pore diameter of 15 to 30 \AA or silica-alumina gel having an average pore diameter of 10 to 20 \AA is formed in pores of an inorganic porous body having pore diameters in the range between 10 and 10000 \AA , and a thin film containing palladium is formed on the surface thereof as a hydrogen permeable film.

[0006] Japanese Patent Laying-Open No. 10-28850 has proposed a hydrogen separation structure including a base material made of porous ceramic or porous

glass, a first layer layered on the base material, and a second layer layered on the first layer and made of Pd or a Pd alloy as a hydrogen permeable film, the first layer being formed of a material having a thermal expansion coefficient within the range between that of the base material and that of the second layer. The first layer relieves stress applied between the base material and the second layer when the hydrogen separation structure is exposed to an atmosphere with large temperature variation, to prevent the second layer from peeling off from the base material.

[0007] Japanese Patent Laying-Open No. 11-267477, Japanese Patent Laying-Open No. 11-286785, or Japanese Patent Laying-Open No. 4-349926 discloses a structure in which a hydrogen permeable film is formed on the surface of a porous support, which has suffered from peeling of the hydrogen permeable film when the hydrogen permeable structure is used in the atmosphere of various conditions, presenting a problem in durability.

[0008] To prevent the hydrogen permeable film from peeling off, the hydrogen separation structure disclosed in Japanese Patent Laying-Open No. 10-28850 has employed a layer, formed of a material having a thermal expansion coefficient within the range between that of a porous base material and that of a hydrogen permeable film, interposed between the porous base material and the hydrogen permeable film.

[0009] By merely relieving the difference in the thermal expansion coefficients between the porous base material and the hydrogen permeable film, however, it was difficult to effectively prevent peeling of the hydrogen permeable film.

[0010] An object of the present invention is, therefore, to provide a hydrogen permeable structure that can more effectively prevent peeling of a hydrogen permeable film and thereby having increased durability, and a method of manufacturing the same.

Disclosure of the Invention

[0011] The present inventors have examined various possible causes of peeling of a hydrogen permeable film, and found that the primary cause of the peeling is the compressive stress occurring at lattice expansion of metallic crystal associated with hydrogen dissolution, rather than the difference in thermal expansion coefficients between a porous base material and the hydrogen permeable film, and that such peeling can be prevented by forming a hydrogen permeable film with a small amount of hydrogen dissolution.

[0012] Based on such findings, a hydrogen permeable structure according to one aspect of the present invention includes a base material including porous ceramic and a hydrogen permeable film formed on the base material, including palladium (Pd) and at least one element other than palladium, and having an amount of hydrogen dissolution at a prescribed temperature small-

er than that of palladium alone.

[0013] Here, the amount of hydrogen dissolution (% by weight) is defined as a value measured according to the method described in the EXPERIMENTAL section of "Solubility of Hydrogen in Palladium-Silver Alloys" in Russian Journal of Physical Chemistry 47(1) published in 1973, and is based on a value measured using a bulk sample with the same composition as the hydrogen permeable film.

[0014] Since the hydrogen permeable structure of the present invention has a hydrogen permeable film with an amount of hydrogen dissolution at a prescribed temperature smaller than that of palladium alone, the amount of hydrogen dissolution into the film can be reduced compared with the structure in which the conventional hydrogen permeable metal film of palladium alone, in the working temperature range including a prescribed temperature. Thus, expansion of the crystal lattice of palladium metal, i.e. expansion of the film, can be suppressed. Therefore, the compression stress of the film occurring by its expansion can be reduced, which can lower the stress applied on the interface between the film and the base material. This can significantly reduce physical deterioration of the hydrogen permeable film such as peeling, crack and the like, and can improve durability of the hydrogen permeable structure.

[0015] Preferably, in the hydrogen permeable structure, the prescribed temperature is at least 200°C and at most 700°C.

[0016] More preferably, in the hydrogen permeable structure of the present invention, the at least one element other than palladium that is included in the hydrogen permeable film is platinum (Pt).

[0017] More preferably, in the hydrogen permeable structure of the present invention, the hydrogen permeable film includes palladium and platinum, the content of the platinum being at least 5% by mass and at most 15% by mass. Increase of the content of platinum can further reduce the amount of hydrogen dissolution into the film, though it lowers the permeability (permeation speed) of hydrogen gas. In order to improve the hydrogen gas permeability to a degree higher than that of the hydrogen permeable structure made of palladium alone and to enhance durability of the hydrogen permeable structure by reducing the amount of hydrogen dissolution into the film, therefore, the content of platinum in the hydrogen permeable film including palladium and platinum is preferably set within the range between 5 to 15% by mass.

[0018] In the hydrogen permeable structure of the present invention, the porous ceramic forming the base material is preferably silicon nitride (Si_3N_4). Among various types of ceramic, silicon nitride is superior in strength, fracture toughness, abrasion resistance, chemical resistance and heat resistance, thereby allowing further enhancement in durability of the hydrogen permeable structure of the present invention.

[0019] The porous base material has a hole on the surface, and a porous oxide layer formed to fill the hole is preferably provided. Thus, the surface of the base material is planarized while the hole at the surface is filled with the porous oxide layer, allowing the hydrogen permeable film to be formed on the surface of the base material in a closely packed manner without pin holes, improving permeability of the hydrogen permeable film. Moreover, adhesion between the surface of the base material and the hydrogen permeable film can be enhanced, allowing further improvement in durability of the hydrogen permeable structure. Here, the oxide layer preferably includes at least one type selected from the group consisting of aluminum oxide (Al_2O_3), silicon dioxide (SiO_2) and zirconium oxide (ZrO_2), and more preferably, is formed of aluminum oxide.

[0020] In a method of manufacturing a hydrogen permeable structure according to another aspect of the present invention, a base material including porous ceramic is prepared, and a hydrogen permeable film is formed on the surface of the base material, including palladium and at least one element other than palladium and having an amount of hydrogen dissolution at a prescribed temperature smaller than that of palladium alone, by a PVD (Physical Vapor Deposition) method.

[0021] In the manufacturing method of the present invention, the surface of the base material is preferably planarized by filling the hole at the surface with a porous oxide layer, and thereafter the hydrogen permeable film is formed on the surface of the base material.

[0022] Furthermore, in the manufacturing method of the present invention, the hydrogen permeable film is preferably formed in the atmosphere with a vacuum of at most 13.3 Pa (0.1 Torr). Here, the potential difference of at least 400V is preferably applied between the base material and a raw material for vapor deposition to form the hydrogen permeable film.

[0023] As described above, according to the present invention, peeling of a hydrogen permeable film and physical deterioration such as cracks can significantly be reduced, improving durability of the hydrogen permeable structure.

Brief Description of the Drawings

[0024]

Fig. 1 shows a schematic cross section of a hydrogen gas separation structure as an embodiment of the present invention.

Best Modes for Carrying Out the Invention

[0025] As shown in Fig. 1, according to an embodiment of a hydrogen permeable structure of the present invention, a hydrogen permeable structure is provided by forming on a porous ceramic base material 1 an alloy film containing palladium and an element other than pal-

ladium, as a hydrogen permeable film 2. The alloy film has an amount of hydrogen dissolution at e.g. 400°C smaller than that of a metal film formed of palladium alone.

[0026] Hydrogen dissolution into palladium metal causes crystal lattice of the palladium metal to expand. The volume of the palladium metal is increased by $2.8 \times 10^{-30} \text{m}^3$ when one hydrogen atom exists in the crystal lattice of the palladium metal. This value and the amount of hydrogen dissolution into the palladium metal film are used to obtain an amount of expansion of the palladium metal film, which is much larger than thermal expansion of the palladium metal film itself when the hydrogen gas separation structure is used at e.g. 400°C. Therefore, in consideration of the combination of the porous ceramic base material and the metal film, reduction in hydrogen dissolution into the film, i.e., inhibition of expansion due to hydrogen dissolution into the film, rather than reduction in thermal expansion of the film itself, can lower the stress applied on the interface between the base material and the film, vastly improving physical deterioration such as film peeling and cracks.

[0027] The hydrogen permeable film may include as a component any elements other than palladium that has an amount of hydrogen dissolution at a prescribed working temperature smaller than that of a film formed of palladium metal alone. An embodiment is to form the hydrogen permeable film by adding platinum to palladium. For example, at the temperature of 400°C, the amount of hydrogen dissolution per 100g of palladium metal is approximately 15mg for the palladium metal alone, whereas, for a palladium-platinum-based alloy comprised of 90% by mass of palladium and 10% by mass of platinum, the amount of hydrogen dissolution per 100g of the alloy is approximately 8mg, which is lower. Moreover, as for hydrogen gas permeability, the amount of hydrogen gas permeation is $2.3 \text{cm}^3/\text{cm}^2/\text{min-cm}$ for the palladium metal alone, whereas it is $2.8 \text{cm}^3/\text{cm}^2/\text{min-cm}$ for the palladium-platinum-based alloy comprised of 90% by mass of palladium and 10% by mass of platinum, showing improvement in the hydrogen gas permeability. It is noted that the measurement is performed under the condition that the temperature is 500°C, the hydrogen pressure on the supplying side is 303.975kPa (3 atmospheric pressure) and the hydrogen pressure on the permeation side is 0kPa (0 atmospheric pressure).

[0028] The hydrogen permeable film may be formed of a single-layer film of an alloy including palladium and an element other than palladium, or may have a multi-layered film structure constituted by a plurality of layers of the alloy above.

[0029] Considering that the hydrogen permeability of the hydrogen permeable film is inversely proportional to the thickness thereof, the thickness of the hydrogen film is preferably at most 10 μm , and more preferably at most 1 μm .

[0030] Moreover, it is preferable to form the hydrogen

permeable film on the surface of a porous ceramic base material that is planarized in such a manner that holes at the surface are filled with aluminum oxide, silicon dioxide, zirconium oxide or the like, to reduce pin holes at the film. More preferably, a porous aluminum oxide layer is formed at a hole portion on the surface of the planarized base material. The surface of the hole portion that has the area ratio of 30-70% is covered by the porous aluminum oxide layer, while ceramic particles are exposed at the surface of the other portion. The hydrogen permeable film formed on the surface of such a base material and the base material are highly adhered to each other. This prevents the hydrogen permeable film from peeling off from the base material when the hydrogen-containing gas is purified, which allows a close structure without pin holes, extremely reducing the amount of gas other than hydrogen passing through the hydrogen permeable film. Therefore, hydrogen gas with high purity can be obtained.

[0031] Though the hydrogen permeable film may be formed by any film-forming method, a method of physically depositing a film with a vacuum of at most 13.3Pa (0.1 Torr), such as an ion plating technique and a sputtering technique, is preferably used to form the film. Here, a potential difference of at least 400V is preferably applied between the base material (or a base material holder) and a raw material for vapor deposition (a target). The application of such a potential difference increases energy used when the raw material for vapor deposition adheres to the base material, improving adhesion of the film to the base material.

[0032] Though there are various types of ion plating techniques and any type thereof may be applied to the present invention, in particular, an arc ion plating technique (arc discharge ion plating technique) is preferably used.

[0033] A film including palladium, for example, has an excellent hydrogen permeability as a hydrogen permeable film. The hydrogen permeability on the (100) plane of the palladium crystal is, however, lower than that of the other crystal planes. Accordingly, a film including palladium is formed such that the palladium crystals are oriented in their (111) planes in order to obtain hydrogen permeability better than that of the film without such orientation. According to the manufacturing method of the present invention, the film including palladium that is formed by applying a potential difference between the base material and the raw material for vapor deposition, palladium crystals are oriented in their (111) planes, so that good hydrogen permeability can be obtained.

[0034] For the porous ceramic used as a base material of the hydrogen permeable structure in the present invention, different types of oxides such as aluminum oxide or various types of nitrides such as silicon nitride may be applied, silicon nitride being the most preferable in terms of strength and the like. The silicon nitride preferably includes therein a net-like cavity portion where columnar $\beta\text{-Si}_3\text{N}_4$ crystal particles are intertangled.

Moreover, the porosity of the porous silicon nitride base material is preferably in the range between 30 and 70%, more preferably in the range between 40 and 50%. Furthermore, the flexural strength of the porous silicon nitride base material is preferably in the range between 30 to 450Mpa, and more preferably in the range between 200 and 450Mpa.

[Example 1]

[0035] A porous silicon nitride sintered body with the average pore diameter of $0.3\mu\text{m}$ was prepared as a base material of a hydrogen permeable structure. Particles of aluminum oxide with the average particle diameter of $0.03\mu\text{m}$ dispersed in water were applied on the surface of the base material and fired at a temperature of 750°C for one hour. Thus, a hole at the surface of the base material was filled with a porous aluminum oxide layer to planarize the surface of the base material.

[0036] An arc ion plating device was used as a device for forming a hydrogen permeable film on the surface of the porous silicon nitride base material processed as described above. An alloy having a composition comprised of 90% by mass of palladium and 10% by mass of platinum, i.e. a raw material for the hydrogen permeable film, was set as a target within a chamber in the arc ion plating device, the base material and the target being spaced by the distance of 300mm. The pressure in the chamber in the arc ion plating device was set to $2.66 \times 10^{-3}\text{Pa}$ ($2 \times 10^{-5}\text{Torr}$) and then the bias voltage and arc current were set at -1000V and 80A, respectively, in order to provide a potential difference between the base material and the target, and the device was operated for 10 minutes. Thus, a palladium-platinum alloy film having a thickness of $0.3\mu\text{m}$ was formed on the surface of the base material.

[0037] For the hydrogen permeable structure manufactured as described above, a heat cycle test was performed 100 cycles at a temperature between 400°C and the room temperature in a hydrogen gas atmosphere of 101.325kPa (1 atmospheric pressure). Subsequent to the test, the film was examined for peeling by visual observation and for cracks by electron microscopic observation, which showed that no physical deterioration of the film such as peeling or cracks was observed. It is noted that the amount of hydrogen dissolution per 100g of an alloy having a composition comprised of 90% by mass of palladium and 10% by mass of platinum was, when measured by the method described earlier, 8mg. Moreover, when 202.65kPa (2 atmospheric pressure) of hydrogen gas was supplied while the hydrogen gas on the permeation side was set as 101.325kPa (1 atmospheric pressure), the amount of hydrogen gas permeation was $100\text{cm}^3/\text{cm}^2/\text{min}$ at the temperature of 350°C .

[0038] Further, when the hydrogen permeable structure was used to purify hydrogen-containing gas at the temperature of 400°C , the palladium-platinum alloy film showed good hydrogen gas permeability without peel-

ing off from the base material, allowing hydrogen gas with high purity to be obtained.

[Comparative Example 1]

[0039] A hydrogen permeable structure was manufactured as in Example 1, except that metal of palladium alone for a raw material of a hydrogen permeable film was set as a target within the chamber in the arc ion plating device. The obtained hydrogen permeable structure was subjected to a heat cycle test under a condition similar to that in Example 1. After ten cycles, the film was examined for peeling by visual observation and for cracks by electron microscopic observation, which showed that partial peeling of the film was observed by visual observation while cracks were observed on the film by the electron microscopic observation. It is noted that, for the metal of palladium alone, the amount of hydrogen dissolution per 100g of metal was 15mg. The amount of hydrogen gas permeation was, when measured under the condition similar to that in Example 1, $50\text{cm}^3/\text{cm}^2/\text{min}$.

[Comparative Example 2]

[0040] A hydrogen permeable structure was manufactured as in Example 1, except that an alloy having a composition comprised of 75% by mass of palladium and 25% by mass of silver for a raw material of a hydrogen permeable film was set as a target within the chamber in the arc ion plating device. The obtained hydrogen permeable structure was subjected to a heat cycle test under a condition similar to that in Example 1. The result revealed that the film was entirely peeled after one cycle of the heat cycle test and completely off the base material. It is noted that the amount of hydrogen dissolution was 75mg per 100g of the alloy having a composition comprised of 75% by mass of palladium and 25% by mass of silver. Because of the peeling, this sample could not be measured for the amount of hydrogen gas permeation.

[Comparative Example 3]

[0041] A hydrogen permeable structure was manufactured as in Example 1, except that metal of palladium alone for a raw material of a hydrogen permeable film was set as a target within the chamber in the arc ion plating device. The obtained hydrogen permeable structure was subjected to a heat cycle test for 100 cycles in atmospheric air of 101.325kPa (1 atmospheric pressure) at a temperature between 400°C and the room temperature. Subsequent to the test, the film was examined for peeling by visual observation and for cracks by electron microscopic observation, which showed that no physical deterioration of the film such as peeling or cracks was observed.

[0042] As described above, comparison between Ex-

ample 1 and Comparative Examples 1 and 2 shows that there is a clear relevance between the amount of hydrogen dissolution into the hydrogen permeable film and durability of the hydrogen permeable structure, and that the hydrogen permeable structure in Example 1 according to the present invention is superior in durability. Moreover, in Comparative Example 3, a heat cycle test was performed in the atmospheric air for the hydrogen permeable structure having a hydrogen permeable film of palladium metal alone, the result of which shows that heat expansion of the film has a small effect on durability of the hydrogen permeable structure, and that it is the expansion of the film due to hydrogen dissolution into the film in hydrogen gas atmosphere that mainly lowers durability.

[0043] It should be appreciated that the embodiments and examples disclosed herein are described by way of illustration, not by way of limitation in all aspects. The scope of the present invention is defined not by the embodiments above but by the claims, and is intended to cover all modifications and variations within the equivalent meaning and scope of the claims.

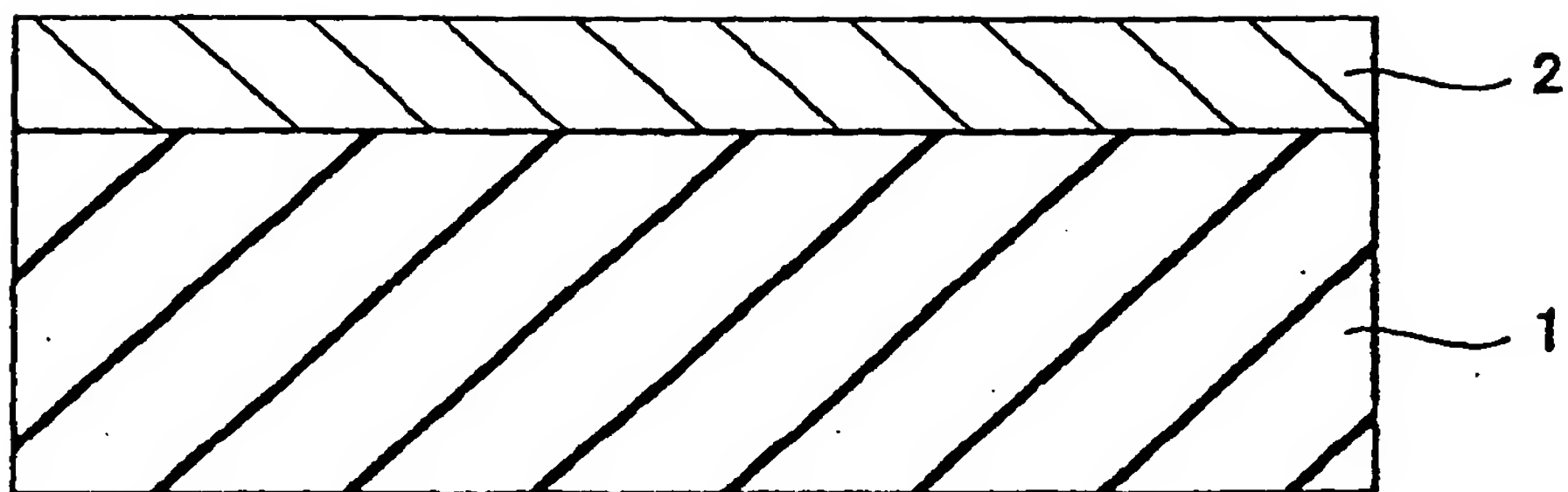
Industrial Applicability

[0044] The hydrogen permeable structure according to the present invention is suitable for obtaining hydrogen gas with high purity for fuel for a fuel cell and the like.

Claims

1. A hydrogen permeable structure, comprising:
 - a base material (1) including porous ceramic, and
 - a hydrogen permeable film (2) including palladium and at least one element other than palladium, and having an amount of hydrogen dissolution at a prescribed temperature smaller than an amount of hydrogen dissolution of palladium alone.
2. The hydrogen permeable structure according to claim 1, wherein said prescribed temperature is at least 200°C and at most 700°C.
3. The hydrogen permeable structure according to claim 1, wherein the at least one element other than palladium is platinum.
4. The hydrogen permeable structure according to claim 3, wherein the content of platinum in said hydrogen permeable film (2) is at least 5% by mass and at most 15% by mass.
5. The hydrogen permeable structure according to claim 1, wherein said ceramic is silicon nitride.
6. The hydrogen permeable structure according to claim 1, wherein said base material (1) has a surface with a hole, and
said hydrogen permeable structure further comprises a porous oxide layer formed to fill in the hole.
7. The hydrogen permeable structure according to claim 6, wherein said oxide layer includes at least one type selected from a group consisting of aluminum oxide, silicon dioxide and zirconium oxide.
8. The hydrogen permeable structure according to claim 7, wherein said oxide layer is formed of aluminum oxide.
9. A method of manufacturing a hydrogen permeable structure, comprising the steps of:
 - preparing a base material (1), on a surface of said base material, including porous ceramic, and
 - forming a hydrogen permeable film (2) on a surface of said base material, including palladium and at least one element other than palladium and having an amount of hydrogen dissolution at a prescribed temperature smaller than an amount of hydrogen dissolution of palladium alone, by a physical vapor deposition technique.
10. The method of manufacturing a hydrogen permeable structure according to claim 9, wherein a surface of said base material (1) is planarized by filling a hole at the surface of said base material (1) with a porous oxide layer, and thereafter said hydrogen permeable film (2) is formed on the surface of said base material (1).
11. The method of manufacturing a hydrogen permeable structure according to claim 9, wherein said hydrogen permeable film (2) is formed in an atmosphere having a vacuum of at most 13.3Pa.
12. The method of manufacturing a hydrogen permeable structure according to claim 11, wherein a potential difference of at least 400V is applied between said base material (1) and a raw material for vapor deposition to form said hydrogen permeable film (2).

FIG.1



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP01/10596

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl. ⁷ B01D71/02		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) Int.Cl. ⁷ B01D71/02		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) WPI/L		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 2000-247605 A (Tokyo Gas K.K.), 12 September, 2000 (12.09.2000), Claims; Par. No. [0018] (Family: none)	1-5, 9, 11, 12
Y	JP 11-57433 A (Tonen Corporation), 02 March, 1999 (02.03.1999), Full text (Family: none)	1-12
A	JP 2000-5580 A (Nippon Metal Industry Co., Ltd.), 11 January, 2000 (11.01.2000), Full text (Family: none)	1-12
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
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